INFLUENCE OF DOPING WITH IRON ON NANOSTRUCTURE FORMATION OF ALUMINUM THIN FILMS ON GLASS SUBSTRATE

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The surface nanostructure of Al and Al-1.5 at.% Fe alloy films obtained by ion-beam-assisted deposition on glass substrates have been investigated by means of scanning probe microscopy (SPM) and scanning electron microscopy (SEM). Analysis of SPM images of the surface of deposited thin films has been performed to plot histograms of the distribution of heights of peaks and valleys of the surfaces. It was revealed that doping with iron increases the morphological heterogeneities of the surface of films. The average roughness of film surface is increased from 23.74 to 38.52 nm with an increase in coating time from 6 to 10 h. Meanwhile, the average diameter of micro-droplets on the surface of films decreases by 1.6 times with increasing the deposition time. The new hybrid parameter *k* was calculated in addition to the ISO roughness parameters to obtain information about the quantitative ratio of the transverse and longitudinal roughness parameters of the nanorelief of samples. The correlation of the film roughness parameters with the size and density of particles of the micro-droplet fraction was established.

Keywords: ion-beam-assisted deposition; scanning probe microscopy; scanning electron microscopy; Al-Fe alloys.

Introduction

Nowadays, thin metal films formed using ion-assisted thin-film coating technologies [1] have become widely spread as reflective, reinforcing, conductive and dielectric coatings. This work aims to study using scanning probe microscopy (SPM) and scanning electron microscopy (SEM) the nanostructure of the coating of Al-1.5 at. % Fe on glass substrates obtained by ion-beam-assisted deposition (IBAD) [2], when during the deposition of a neutral metal fraction the formed film is irradiated by ions of the ionized metal fraction. The selection of Al–Fe alloy system is determined by the prospects of expanding the field of application of aluminum-based materials in nanotechnology, as well as optical films of metals on glass substrates for modern electronics and solar photoenergy devices [3].

In addition to the amplitude parameters of roughness, quantitative information about the transverse (height) and longitudinal characteristics of the nanorelief was obtained during the analyzing the surface morphology of samples using SPM. The presented analytical approach to the description of the structure of samples on basis of SPM imaging includes the determination of ISO roughness parameters for films and the experimental data approximation with the normal distribution law. The research hybrid coefficient *k* is proposed to be used in addition to diagnose the surface quality of the film/substrate system and assess changes in the shape of the irregularities of the nanorelief profile [4].

Materials and research methods

Ion-beam-assisted deposition of films of aluminum (99,995) and its Al-1.5 at. % Fe alloy was carried out using a resonance ion source of vacuum arc plasma ($P = 10^{-2}$ Pa) at an accelerating voltage *U*=3.0 kV, an ion current of ~ 100 μA, a current density of 5.1 μA / cm^{-2}, and a deposition rate of ~ 0.1-0.2 nm / min. The deposition time of Al film was 10 h, while the time of coating formation for Al–Fe alloy was 6 h and 10 h. The calculated values of the thicknesses of Al-Fe alloy films were 50 and 90 nm, respectively. The nanostructure of the films was studied using SPM on an NT-206 atomic force microscope (AFM) and SEM on a LEO1455VP microscope with "HKL CHANNEL5" backscattered electron diffraction camera. The average diameter $\overline{D}$, the volume fraction *V*, and the specific surface area of the boundaries S_{sp} of the droplet fraction of microparticles on the surface of samples were determined by the secant method.

The amplitude roughness parameters such as average roughness R_a and the root-mean-square roughness R_q were measured for samples using SPM data and image processing by *SurfaceXplorer* software. Taking into account the aperiodicity of the structural elements of the surface nanorelief of metal films, a new hybrid research parameter was calculated, depending on both the amplitude and spacing roughness: parameter $k = R_z/S$, where 10-point height of profile irregularities R_z is the amplitude roughness parameter, mean spacing of adjacent local peaks S is the spacing roughness parameter. Since the *SurfaceXplorer* software does not calculate R_z and also does not allow to determine the spacing parameters of roughness, an algorithm for analyzing and statistical processing of SPM data was additionally developed and implemented using the *Microlab Origin* software package and *MS Excel*. Analytical determination of parameter k was implemented by calculating the R_z and S parameters using standard formulas [4,5]. Once a measurement of R_a parameter for each separate specimen required to obtain SPM data for at least 5 surface areas of the film, the parameter k was determined for the area, the roughness of which matched the averaged value of the R_a. Note, the parameter of the average roughness was chosen to verify the accuracy of the results of introduced analytical processing. The maximum difference between the results obtained for R_a by these two approaches (analytical one and *SurfaceXplorer* software) was within $\pm 5\%$.

Results and their discussion

It was found that the surface of a typical glass substrate has a fine-element morphology and exhibits slight surface roughness (R_a=0.17 nm, R_q=0.22 nm) as well as a considerable uniformity of roughness across the entire area of the specimen. The ion-beam-assisted deposition of films on glass substrates results in the formation of surfaces, the roughness of which is determined by irregularities of different geometric types with varying degrees of heterogeneity depending on the element composition of the samples and deposition time.

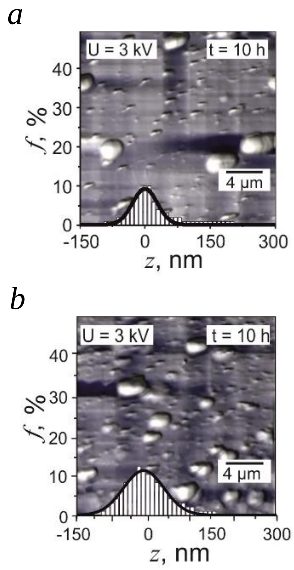


Fig. 1. SPM images of thin films of Al (*a*) and Al-1.5 at.% Fe alloy (*b*) deposited on glass substrate (*U*=3 kV, *t*=6 h) and the corresponding distribution histograms of heights of peaks and valleys of the surface nanorelief

SurfaceXplorer software was used to analyze the captured SPM images: extract the *x*-*z* coordinates of the roughness profiles and calculate roughness parameters R_a, R_q, R_z and S for glass substrate and films deposited under different conditions. The parameters that characterize the morphological features of the surface of glass substrate and films are shown in Table 1. A typical SPM image of the surface

Table 1. Values of parameters describing the morphology and topography of glass substrate, films of Al and Al–Fe alloy deposited on the glass substrate

Sample	t, h	R_a, nm	R_q, nm	k, 10^{-2}	$\bar{D}$, μm	V, %	S_{sp}, 10^{-2} μm^{-1}
Glass substrate	-	0.17	0.22	0.04	-	-	-
Al (99.995)	10.0	31.51	51.52	2.53	0.88	5.45	20.21
Al–1.5 at. % Fe	6.0	23.74	37.09	1.2	1.02	2.83	9.14
Al–1.5 at. % Fe	10.0	38.52	58.33	3.2	0.62	4.05	21.44

of Al–Fe alloy film deposited on glass substrate at U=3 kV for 6 h is illustrated in Fig. 2*a*. For each samples Within the sampling length the roughness profiles $z(x, y)$ were plotted along 11 horizontal lines (labeled from 1 to 11) drawn with an interval 2 μm parallel to the X-axis to calculate the roughness parameters R_a, R_z and S in respect to the middle line of each profile.

Figure 2*b* shows an example of the roughness profile for film surface of Al–Fe alloy (U=3 kV, t=6 h), extracted by scanning along the line labeled with the number 2 in SPM image in Fig. 2*a*. For comparison, Fig. 2*b* presents additionally two roughness profiles extracted for Al film and Al–Fe alloy deposited during 10 h, see Fig. 1. It demonstrates the case when roughness profiles with different shapes of irregularities extracted along the selected lines on the surface of different samples have almost the same value of average roughness (R_a ~ 30 nm).

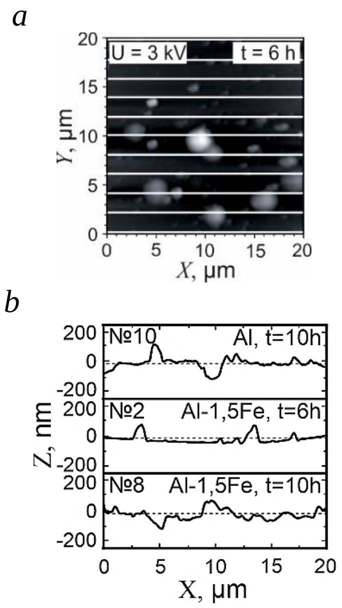


Fig. 2. SPM image of Al–1.5 at.% Fe alloy film (U=3 kV, t=6 h) with surface scan lines (*a*) and roughness profiles of films deposited on glass under different conditions (*b*)

To quantify the height distribution of the nanorelief elements on the film surface, a statistical analysis of the intersections of the extracted roughness profiles with auxiliary secants drawn with an interval 10 nm parallel to the X-axis was performed for each labeled scan line, and the corresponding histograms were obtained, see Fig. 3*a*. The resulting histogram of the distribution over the size groups of the average measured values of the heights of peaks and valleys of the sample surface nanorelief was constructed by averaging of data of 11 histograms obtained for selected samples of each composition, see Fig. 3*b*. For comparison, the correspondent histogram provided by *SurfaceXplorer* software for the same film is shown in Fig. 3*c*.

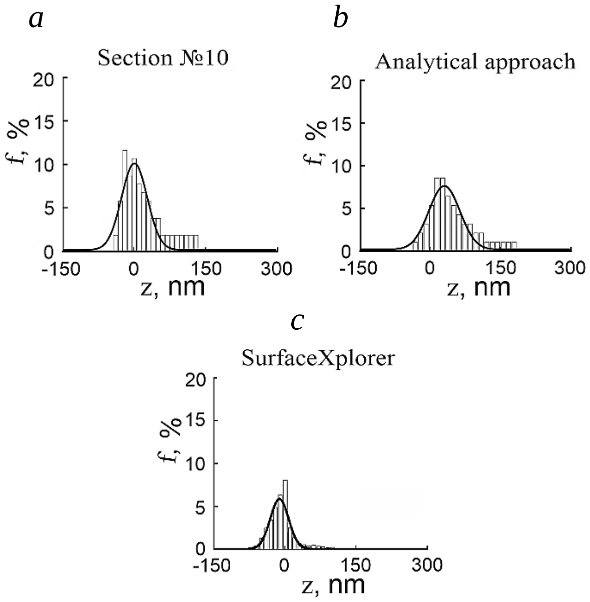


Fig. 3. Histograms of the distribution of heights of peaks and valleys of Al–1.5 at.% Fe alloy film (U=3 kV, t=6 h) shown in Fig. 2a: *a* – histogram of the roughness profile plotted along the scanning line No. 2, *b* and *c* - spatial nanorelief of the film surface with an area of 20x20 μm^2, determined using analytical processing of SPM data and application *SurfaceXplorer* software, respectively

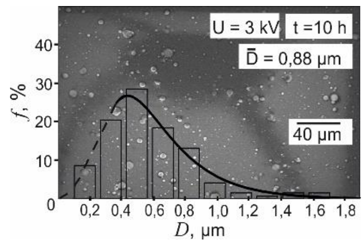
As can be seen from Figs. 1 and 3, height histograms of films obtained using ion-beam-assisted deposition are unimodal, have a pronounced maximum and can be approximated by a normal (Gaussian) distribution. At the same time, some asymmetry of the histogram in the area of positive z values indicates a large number of local maxima relative to the middle line of the roughness profile in comparison with the Gaussian distribution. In particular, the root-mean-square roughness R_q, which characterizes the width of the height/depth distribution histogram, is increased if the film surface is coarser.

The measured analytically roughness parameters R_z and S allowed to calculate the hybrid parameter k, which characterizes the spatial heterogeneity of the nanorelief of film surface. For Al-1.5 at.% Fe alloy films on glass substrate, it was found that there is the trend of increasing k along with the increase of average roughness R_a, see Table 1. With an increase in the deposition time from 6 h to 10 h, the surface of Al–Fe alloy films becomes more rough (value of R_a is in 1.6 times higher), and the k parameter increases by 2.7 times and reaches a value of $3{,}2 \cdot 10^{-2}$. Taking into account that there is a linear correlation between the parameters R_z and R_a, the next statement can be drawn: the distance between the protrusions of the profile irregularities decreases with increasing film thickness in the case of longer time of the film deposition, see Figs. 1*b* and 2*a*. Thus, k provides additional information about the shape of the surface irregularities across the area of the film and is in line with followed SEM data.

Figure 4 shows typical SEM images of thin films of Al and the Al–1.5 at. % Fe alloy deposited on glass substrate. It was found that these films are coatings without deformations. The characteristic roughness indicates that the surface of films has an island character. There are microparticles of the droplet fraction from the cathode material on the film surface, the size of droplets depends on the deposition time of the films. Most microparticles are spherical in shape. It was found that when aluminum is alloyed with iron, the volume fraction of microparticles on the surface of films deposited in 10 hours decreases by 25%. The specific surface area of the boundaries S_{sp} of the microparticles of the droplet fraction depends directly on time: it increases with increasing time. Thus, with an increase in the deposition time from 6 h to 10 h micro-droplet fraction increased by 2.3 times. At the same time, for the samples of the Al film and the Al-Fe alloy film, which were deposited during the same time (t=10 h), S_{sp} has almost the same values.

These results are explained by the fact that the specific surface area of the boundaries S_{sp} of microparticles of the droplet fraction depends on their diameter and volume fraction. In particular, it can be concluded that the number of droplets as well as their density increases with the decrease in their diameters. The diameter of droplet fraction microparticles on the film surface of Al–Fe alloy is considered to be lowered (t=10 h) due to the immuring of previously deposited microparticles as the film grows at longer film deposition times. It was established that the frequency curves of the distribution of the sizes of microparticles demonstrate a distinct positive deviation from the normal law and are satisfactorily described by lognormal distribution with the coefficient of determination COD (R^2) 0.72-0.95.

a



b

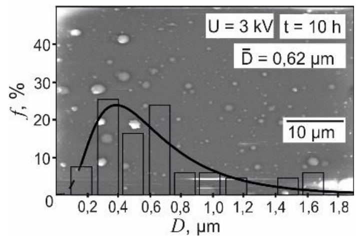


Fig. 4. SEM images of the surface of thin films of Al (*a*) and Al-1.5 at.% Fe (*b*) deposited on glass substrate with corresponding histograms of the size distribution of microparticles of the droplet fraction

As it is followed from Table 1, the nanostructure of the surface of films on a glass substrate is changed markedly when Al is doped with Fe. The uneven filling of the depressions and protrusions of the initial relief of the glass substrate at the initial stage of deposition of Al film leads to the fact that, if the average roughness R_a of the glass substrate is 0.17 nm, then for the Al film the value R_a is 31.51 nm. A comparison of the values of the parameters characterizing the roughness amplitudes of the films in Table 1 shows that as a result of Al doping with Fe, the degree of morphological heterogeneity of the surface of the alloys increases. Additionally, the linear dependence of the hybrid parameter k on R_a is determined. In particular, this indicates that in the case of Al–Fe alloy deposition on glass, with increasing deposition time the distance between the protrusions of the terrain profile irregularities is decreased because despite the decrease in the size of micro-droplets their density is increased.

In this work, the deposition of thin films was performed by IBAD, the distinctive advantage of which is the use of ions of the deposited metal as assisting ions. The surface morphology of films plays an extremely important role in controlling the complex of surface properties of coatings, which are determined not so much by the characteristics of the material as a whole, but by the structure and properties of the surface layers of the coating/substrate system, both at the nano- and submicron scales. The revealed regularities of the structure film formation of Al doped with Fe indicate the prospects of further study the relationship between the roughness parameters and the physicochemical properties of the films formed during hyperspeed crystallization on glass substrates when the composition of the coatings and the conditions of deposition are modified.

Conclusion

As a result of the study of the surface nanostructure of thin films of Al and Al–Fe alloy on glass substrates, the roughness parameters and the regularities of the micro-droplet size distributions were determined. It is found that the degree of morphological inhomogeneity of the surface of the films under iron doping increases in comparison with films of clean Al. At U=3.0 kV (t=10 h), R_a is 38.52 nm, which is 20% higher than the average roughness of the pure Al film (R_a =31.51 nm). When aluminum is alloyed with iron, the average diameter and volume fraction of microparticles on the surface of films deposited in 10 hours are reduced by 30% and 25% respectively compared to Al films. Histograms of the distribution of heights of peaks/valleys of the surface of films are unimodal and can be satisfactorily described by the Gaussian distribution. The frequency distributions of the micro-droplet fraction by size have a lognormal character. It was shown how analytical processing of the surface images of thin films obtained using SPM makes it possible to determine the value of the hybrid parameter k and obtain quantitative information about the transverse and longitudinal characteristics of the surface roughness, as well as the distribution of the heights and valleys of the nanorelief, depending on the composition and conditions of the coating deposition.

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